5262 *J. Am. Chem. Soc.* **1980**, *102*, 5262–5265

Generation of Arenium Ions by a Self-Protonation Reaction in an Aprotic Molten Salt Medium

A. C. Buchanan, III,* A. S. Dworkin, and G. P. Smith

Contribution from the Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830. Received February 4, 1980

Abstract: We have examined the reaction behavior of a group of polycyclic aromatic hydrocarbons in the aprotic liquid $SbCl_3$–10 mol % $AlCl_3$ from 100 to 130 °C by ^1H NMR and by quench and separation techniques. For anthracene, pyrene, 9,10-dimethylanthracene, 9,10-diphenylanthracene, and naphthacene, we have observed a novel arene self-protonation reaction for which the proton source is the condensation–dehydrogenation of a portion of the arene combined with arene oxidation by $SbCl_3$. Naphthalene and phenanthrene, however, do not undergo this reaction. Evidence is presented which indicates that the self-protonation reaction proceeds through the oxidation of the arene to its radical cation by $SbCl_3$, and that the function of $AlCl_3$ is to enhance the oxidizing power of the Sb^{3+}/Sb^0 couple.

Introduction

Previously, the protonation of anthracene and similar arenes has only been achieved by supplying strong proton donors such as superacid media[1] or $AlCl_3$–HCl.[2] However, in a communication we reported[3] that the dissolution of anthracene in the aprotic liquid $SbCl_3$–10 mol % $AlCl_3$ at 100 °C resulted in the formation of stable solutions of the 9-anthracenium ion (**1**). We demonstrated that the proton source for this reaction was the condensation–dehydrogenation of a portion of the anthracene, and that the reaction was driven by the reduction of $SbCl_3$ to antimony metal. The presence of $AlCl_3$ was necessary for this reaction to occur, since anthracene and other arenes in molten $SbCl_3$ (mp 73.2 °C) without $AlCl_3$ undergo a catalytic hydrogen redistribution reaction with the formation of hydroaromatics and Scholl condensation products.[4,5] In this article, we present a full account of this unusual self-protonation reaction including a description of the reaction behavior of a group of arenes [naphthalene, phenanthrene, pyrene, anthracene, 9,10-diphenylanthracene (DPA), 9,10-dimethylanthracene (DMA), and naphthacene] of widely varying basicity and oxidizability.

Experimental Section

Materials. The organic compounds used for this study were commercial reagents of the highest available quality (99+ to 99.9+%). DPA and DMA were used without further purification. The other arenes were sublimed before use, and anthracene was also recrystallized first from acetic acid and then from toluene before sublimation. The purity of these organic reagents was confirmed by UV, GC, or LC.

$SbCl_3$ was further purified from anhydrous material obtained from three different vendors—Apache (99.999%), Atomergic Chemetals Co., Div. Gallard-Schlesinger (99.999%), and Ventron-Alfa (99.99%). The $SbCl_3$ was first refluxed over antimony metal, Apache (99.999%), in an argon atmosphere to reduce any $SbCl_5$ which might be present to $SbCl_3$. Sublimation under vacuum at 40 °C followed by distillation under a reduced pressure of argon at 95 °C gave a white solid which melted to a clear, colorless liquid. Spark source mass spectrometry did not detect any inorganic oxidizing impurities above 2 ppm.

$AlCl_3$ was prepared according to a published procedure[6] from zone refined 99.9999% aluminum metal (Cominco Products, Inc.) and specially prepared HCl, yielding a colorless solid.

$(CH_3)_4NCl$ was purified from 99+% material (Matheson Coleman and Bell) by precipitation from a hot methyl alcohol–acetone solution upon addition of acetone. The precipitate was filtered and the operation repeated in Schlenk-ware under an argon atmosphere. The product was then dried under vacuum at room temperature.

Manipulation of Reagents. All material transfers were performed in a controlled atmosphere glovebox. The argon atmosphere in this box was constantly circulated through a purification system and continuously monitored for moisture and oxygen content, which amounted to 1 ppm each.

NMR. Reactions were studied in situ in 5-mm-o.d. NMR tubes (1-mm wall) filled with 0.7–1.2 g of $SbCl_3$, 0.045–0.065 g of $AlCl_3$, and 0.020–0.040 g of the arene. The tubes were filled in the glovebox and subsequently sealed under argon on a vacuum line. A 10 mol % $AlCl_3$ concentration was always employed. For the self-protonation reaction to proceed, the presence of excess $AlCl_3$ was necessary and in our experiments the $AlCl_3$/arene mole ratio was 2 or more.

The ^1H NMR experiments were done at temperatures from 100 to 130 °C on either a Varian XL-100 spectrometer with a ^{19}F external lock or a Varian FT-80 spectrometer with ^2H external lock. The formation of the arenium ions in the melt was studied both with and without $(CH_3)_4N^+$ as an internal standard for quantitative measurements. The chemical shifts were also referenced internally to $(CH_3)_4N^+$ (δ 3.12), which was itself separately referenced to Me_4Si both in the melt and in D_2O.

Separation and Identification. Products were identified from larger scale reactions (up to 0.5 g or 5 mol % of the arene) performed in Schlenk glassware under argon for 30–45 min. In the case of anthracene, the reaction products were also separated from the in situ NMR experiments and found to be identical with those identified from the larger scale reactions.

The reaction mixture was hydrolyzed in 6 M HCl and the organics were dissolved in CH_2Cl_2 under argon. The mixture was filtered and the solid which remained (if any) was thoroughly washed with 6 M HCl and CH_2Cl_2. Any solid left on the filter was reacted with a 3:1 HCl–HNO_3 (v/v) mixture, and the resulting solution was analyzed for antimony metal with an Instrumentation Laboratory atomic absorption spectrometer. The CH_2Cl_2 layer was separated from a CH_2Cl_2/HCl workup, and the solvent was removed on a rotary evaporator.

The primary method for analysis of the major organic products was LC on a Waters liquid chromatograph which had a variable wavelength UV detector and a gradient elution solvent programmer. A Whatman Partisil M9-ODS-2 reverse phase column and a CH_3OH–H_2O or CH_3OH–CH_2Cl_2 solvent system were used. Collected fractions were characterized by their UV and/or mass spectra. Quantitative yields were determined by UV spectroscopy on a Cary 14 spectrophotometer. Some analyses were also performed on a Bendix gas chromatograph with a flame ionization detector and a column containing Dexsil 400 on 80/100 mesh Chromosorb G-HP.

Independent Preparation of Some Arenium Ions. To aid in the NMR identification of the protonated arenes from anthracene, naphthacene, pyrene, and DPA which were generated in the $SbCl_3$–$AlCl_3$ melt, these arenium ions were also prepared by the procedure of Koptyug.[2] This involved the Schlenk-ware reaction under argon of the arene with $AlCl_3$ and HCl gas in benzene as solvent. Removal of the benzene under vacuum gave the arenium ion as a chloroaluminate salt. The salt was transferred into a glovebox from which samples were prepared for the NMR studies as described above.

The ^1H NMR spectrum of each arenium salt was measured in $SbCl_3$, $SbCl_3$–10 mol % $AlCl_3$, and $AlCl_3$–NaCl–KCl (60:26:14 mol %). The chemical shifts measured in these solvents were constant to within ±0.1 ppm. In addition, the ^1H NMR spectrum of the anthracenium salt was

---

[1] Olah, G. A.; Staral, J. S.; Asencio, G.; Liang, G.; Forsyth, D. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6299.

[2] Koptyug, V. A.; Isaev, J. S.; Rezvukhin, A. I. *Tetrahedron Lett.* **1967**, 823.

[3] Buchanan, A. C., III; Dworkin, A. S.; Brynestad, J.; Gilpatrick, L. O.; Poutsma, M. L.; Smith, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 5430.

[4] Dworkin, A. S.; Poutsma, M. L.; Brynestad, J.; Brown, L. L.; Gilpatrick, L. O.; Smith, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 5299.

[5] Poutsma, M. L.; Dworkin, A. S.; Brown, L. L.; Benjamin, B. M.; Smith, G. P. *Tetrahedron Lett.* **1978**, 873.

[6] Bjerrum, N. J.; Boston, C. R.; Smith, G. P. *Inorg. Chem.* **1967**, *6*, 1162.

0002-7863/80/1502-5262$01.00/0

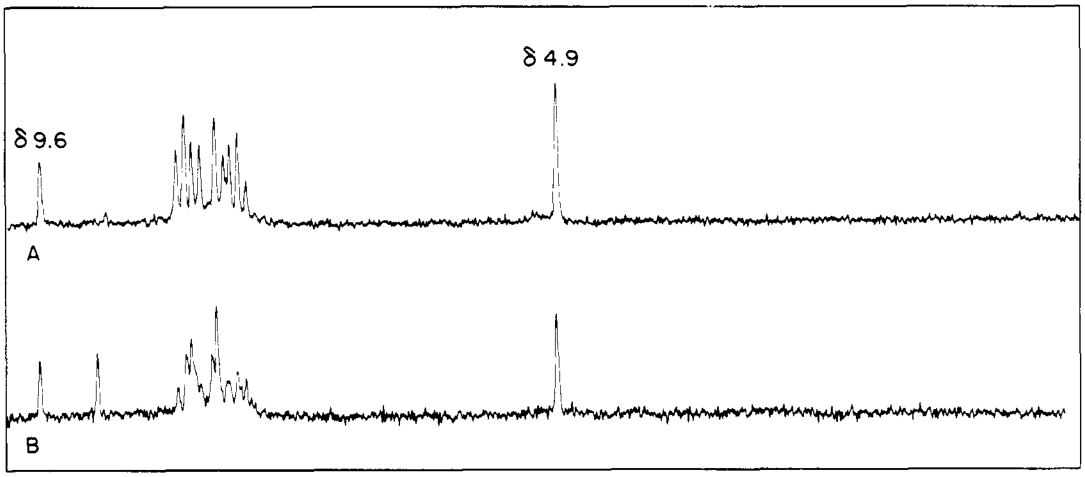
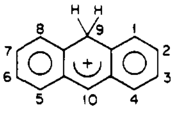


Figure 1. ^{1}H NMR of some arenium ions formed in $SbCl_3$–$AlCl_3$ at 100 °C: (A) anthracenium; (B) naphthacenium.

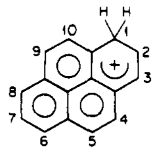
measured as a 45% solution in benzene and was consistent with the literature spectrum reported in benzene.[2] In this case, the NMR resonances were shifted ~0.8 ppm upfield compared to those observed in the molten salt solvents described above.

Results

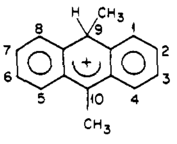
Anthracene, Pyrene, DMA, and Naphthacene. The dissolution of anthracene, pyrene, DMA, and naphthacene in $SbCl_3$–10 mol % $AlCl_3$ at 100 °C gave, by ^{1}H NMR, the prompt formation (<10 min) of stable solutions of the corresponding protonated arenium ions [anthracenium (**1**), pyrenium (**2**), 9,10-dimethylanthracenium (**3**), and naphthacenium (**4**)] in 55–65% yields. The NMR spectra for the molten salt solutions of **1**, **3**, and **4** remained unchanged for several hours at 100–130 °C. Although the solutions of **2** in $SbCl_3$–$AlCl_3$ were stable at 100 °C, NMR showed that this ion slowly decomposed at 130 °C. This phenomenon was also observed for the molten salt solutions of authentic **2** (vide infra) and is perhaps a result of the weaker proton basicity of pyrene compared to those of anthracene, naphthacene, and DMA.[7]



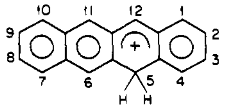
1



2



3



4

The identities of **1** and **3** were confirmed from their published ^{1}H NMR spectra.[1,2,8] The identities of **2** and **4** were confirmed, and that of **1** was reconfirmed, from a comparison of their respective integrated ^{1}H NMR spectra with those obtained from authentic samples of **1**, **2**, and **4** (see Experimental Section) in $SbCl_3$ without extra $AlCl_3$. The NMR spectra of these authentic arenium ions were the same whether the solvent was $SbCl_3$, $SbCl_3$–10 mol % $AlCl_3$, or $AlCl_3$–NaCl–KCl (60:26:14 mol %).

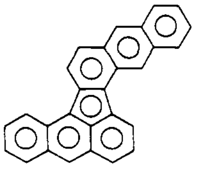
Representative NMR spectra are shown in Figure 1 for **1** and **4** in molten $SbCl_3$–$AlCl_3$. The prominent feature in the spectra of arenium ions **1**–**4** is the presence of a midfield peak resulting from the conversion of an sp^2- to an sp^3-hybridized carbon upon protonation. The chemical shifts for **1**–**4**, including those for the midfield peaks, are given in Table I. For cation **2**, the chemical shift for the aliphatic CH_2 is the only portion of the spectrum reported in the literature,[9] and it is in agreement with our value (Table I). We also observe in the spectrum a downfield shift of four protons which we attribute to a roughly equal distribution of the positive charge over $H_{5,6,8,9}$ in what can be considered a substituted perinaphthenyl cation.[10] The spectrum of cation **4** does not appear in the literature. By analogy with the NMR spectrum of **1**, we assign the absorption at δ 9.6 to H_{12}, and the absorption at δ 9.1 was assigned to H_{11} from a consideration of possible resonance forms.

Table I. ^{1}H NMR Chemical Shifts for Some Arenium Ions in Molten $SbCl_3$–10 mol % $AlCl_3$[a]

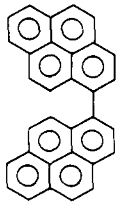
	aliphatic[b]	aryl
1	H_9 (s) = 4.9	H_{10} (s) = 9.6; H_{1-8} (m) = 7.6–8.5
2	H_1 (s, br) = 4.4	$H_{5,6,8,9}$ (s, br) = 8.8;[c] $H_{2-4,7,10}$ (m) = 7.5–8.3
3	H_9 (s, br) = 4.7[d]	H_{1-8} (m) = 7.5–8.6
4	H_5 (s) = 4.9	H_{12} (s) = 9.6;[c] H_{11} (s) = 9.1;[c] $H_{1-4,6-10}$ (m) = 7.6–8.6

[a] Chemical shifts are in parts per million from Me_4Si. Multiplicities are in parentheses: s = singlet, m = multiplet, br = broad. [b] For protons on the sp^3-hybridized carbons. [c] See text for assignment. [d] CH_3 on C-9 (s, br) = 1.6; CH_3 on C-10 (s) = 3.6.

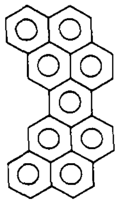
The source of the protons in these reactions is the condensation–dehydrogenation of a portion of the arene combined with arene oxidation by $SbCl_3$. The organic products were separated by quench and workup procedures performed on the melt. In each case, a number of condensed products were observed in the LC of the recovered organics. For anthracene, the primary condensed product (~21% by weight) was anthra[2,1-*a*]aceanthrylene (**5**). The identity of **5** was confirmed from its mass spectrum (mass 352) and a comparison of its melting point and complex UV spectrum with literature values.[4] In the case of pyrene, the principal condensed products were the bipyrenes, 1,1′-bipyrene (**6**) and dinaphtho[2,1,8a,8,7-*defg*:2′,1′,8a′,8′,7′-*ijkl*]pentaphene (**7**). The identification of **6** and **7** (each formed in ~10% by



5



6



7

---

[7] Mackor, E. L.; Hofstra, A.; van der Waals, J. H. *Trans. Faraday Soc.* **1958**, *54*, 66, 186.

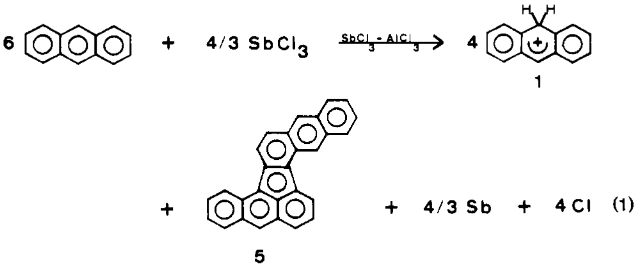
[8] MacLean, C.; Mackor, E. L. *Mol. Phys.* **1961**, *4*, 241.

[9] MacLean, C.; van der Waals, J. H.; Mackor, E. L. *Mol. Phys.* **1958**, *1*, 247.

[10] Streitwieser, A., Jr.; "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961; p 358.

weight) was based on a comparison of their UV spectra with those reported in the literature.[11] For DMA, the main condensed product was found to have a mass of 424 from mass spectroscopy, which indicated the incorporation of an "extra" methyl group in a bianthracene-type molecule. Consistent with this finding was the observation of about 8% 9-methylanthracene in the organic product mixture. Several other condensed products were observed in the LC, but all in small amounts. The condensed organic products from the naphthacene reaction were not analyzed because of the extremely low solubility of naphthacene and its condensed products in organic solvents. The NMR spectra of the condensed products from these reactions were not resolved in the in situ NMR experiments. They appeared as extra absorption in the aromatic region underneath the spectra of the arenium ions.

A typical overall reaction for the condensation–protonation reaction of these arenes in $SbCl_3$–$AlCl_3$ is shown in eq 1 for anthracene in terms of its principal condensed product, **5**. For



anthracene, pyrene, and DMA, the amount of Sb metal found followed the stoichiometry of $^1/_3$ mol of Sb^0 for every 1 mol of arenium ion produced (as in eq 1). In the case of naphthacene, the amount of Sb^0 detected was variable and less than the stoichiometric quantity generally found in these reactions, perhaps owing to the solubility problems encountered during workup of the melt.

For the anthracene reaction, the black antimony powder was further analyzed by X-ray diffraction and found to be amorphous. Amorphous Sb metal has been previously observed but reported to be thermally unstable.[12] We found that heating a sample of the amorphous material in a sealed capillary under argon for 18 h at 350 °C converted the amorphous Sb to its normal rhombohedral structure.

From eq 1 it is clear that the amount of protonated arene formed in the self-protonation reaction depends on the type of condensed products that are generated. For example, the formation of a product (or products) such as **6** with one bond between the aryl moieties liberates two protons leading to the formation of ~50% (by weight) arenium ion. If condensed products are formed with two bonds between the aryl groups, as in **5** and **7**, then four protons are released producing ~67% arenium ion. Consistent with the observed condensed products we always found between 55 and 65% protonated arene.

DPA, Naphthalene, and Phenanthrene. The NMR of a solution of DPA in $SbCl_3$–$AlCl_3$ at 100 °C showed the initial formation of the protonated 9,10-diphenylanthracenium ion (**8**) as indicated by a midfield peak for the aliphatic hydrogen at δ 5.0 and from a comparison of the spectrum with that of a sample of **8** prepared by the Koptyug procedure (see Experimental Section). However, the NMR spectrum was not constant with time, and a sharp singlet at δ 7.3 (the chemical shift for benzene) grew in rapidly. The spectrum of authentic **8** in the melt was stable at 100 °C for 45 min, but at 130 °C the resonance at δ 7.3 grew in rapidly. These results suggest that the unusual behavior of DPA in the $SbCl_3$–$AlCl_3$ melt, compared to anthracene and DMA, can be ascribed to the presence of the phenyl groups. It appears that the protonated DPA reacts further in the melt with the resultant cleavage of a phenyl–anthracene bond of a type that has been previously described.[13]

We found by NMR that naphthalene and phenanthrene underwent very little reaction in molten $SbCl_3$–$AlCl_3$ for a period of about 30 min at 100 °C. However, after 2 h at 100 °C or 25 min at 130 °C, both compounds had reacted extensively and the NMR showed many overlapping resonances in the aliphatic region from ~1 to 5 ppm. The analysis of the products from a larger scale naphthalene reaction (25 min at 130 °C) by GC–MS showed the presence of several hydrogenated arenes (not found in the self-protonation reactions) such as tetralin, as well as Scholl condensation products. Furthermore, no Sb metal was detected in this reaction. These results indicate that the condensation–protonation reaction did not occur for naphthalene and phenanthrene in the melt but, instead, a catalytic hydrogen transfer reaction took place of the type we reported earlier.[4]

Discussion

In the experiments described here, arenes were protonated in an aprotic medium in amounts that cannot be accounted for by protonic impurities. Thus, a portion of the arene must have first reacted to form a strong protonic acid which then protonated the rest of the arene. In this section we address the question of what this acid might have been and how it may have been formed.

In an earlier study[4] we showed that anthracene and naphthacene in $SbCl_3$ without $AlCl_3$ undergo hydrogen redistribution reactions to form hydroaromatics (not found in the presence of excess $AlCl_3$) and condensed aromatics. In addition, reduction of the $SbCl_3$ solvent was not observed. We have since observed a similar reaction for DMA. Under the same conditions we found naphthalene, phenanthrene, pyrene, and DPA to be unreactive. In the present study we found that, when a substantial excess of $AlCl_3$ is added to the above systems, naphthalene and phenanthrene (the least basic and least easily oxidized of the hydrocarbons studied) remain inert or undergo hydrogen-transfer reactions, depending on the temperature, while the other five hydrocarbons undergo condensation/self-protonation reactions accompanied by reduction of $SbCl_3$ as typified by eq 1.

Aluminum chloride is an exceptionally strong chloride ion acceptor so that, qualitatively, one would expect it to enhance the reduction of $SbCl_3$ by reacting with the Cl^- released through the reduction of $SbCl_3$.[14] This effect was studied quantitatively by Bauer and co-workers,[15,16] who measured the formal potential of the Sb(III)/Sb couple in molten $SbCl_3$ at 99 °C as a function of the formal concentrations of $AlCl_3$ and a strong Cl^- donor, KCl or triphenylmethyl chloride. These workers also measured the anodic $E_{1/2}$ values for the oxidation to radical cations of a series of arenes in molten $SbCl_3$.[17] They concluded that, when the oxidizing power of $SbCl_3$ is enhanced by the addition of moderate amounts of $AlCl_3$ (e.g., 10 mol %), a number of arenes including anthracene, DMA, DPA, and naphthacene should be oxidized by the solvent at 99 °C to radical cations. Although these workers did not study naphthalene or phenanthrene, it may be inferred from $E_{1/2}$ values in other media[18] that they should not be oxidized to any significant extent by molten $SbCl_3$–10 mol % $AlCl_3$. These conclusions, based on electrochemistry, are supported by our ESR study[19,20] of the oxidation of arenes in $SbCl_3$ with and without

---

[11] Clar, V. E.; Kühn, O. *Justus Liebigs Ann. Chem.* **1956**, *601*, 181.

[12] Smith, J. D. "The Chemistry of Arsenic, Antimony, and Bismuth"; Pergamon Press: Elmsford, N.Y., 1973; p 552.

[13] Koptyug, V. A.; Bushmelev, V. A.; Gerasimova, T. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1967**, *37*, 127.

[14] Molten $SbCl_3$ is generally regarded as a leveling solvent for strong Lewis acids like $AlCl_3$, which are believed to react and form an equivalent amount of $SbCl_2^+$. For example, see ref 15–17.

[15] Bauer, D.; Texier, P. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1968**, *266*, 602.

[16] Texier, P. *Bull. Soc. Chim. Fr.* **1968**, 4716.

[17] (a) Bauer, D.; Beck, J. P.; Texier, P. *Collect. Czech. Chem. Commun.* **1971**, *36*, 940. (b) *C. R. Hebd. Seances Acad. Sci., Ser. C* **1968**, *266*, 1335.

[18] For example, in propylene carbonate, see: Madec, C.; Courtot-Coupez, J. *J. Electroanal. Chem.* **1977**, *84*, 177.

[19] Buchanan, A. C., III; Livingston, R.; Dworkin, A. S.; Smith, G. P. *J. Phys. Chem.* **1980**, *84*, 423.

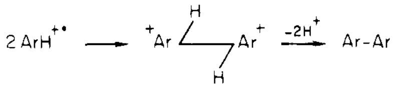
[20] According to Bauer and co-workers[17] the difference between $E_{1/2}$ for pyrene and the formal $E(Sb^{3+}/Sb)$ for $SbCl_3$ containing on the order of 8–10 mol % $AlCl_3$ is a little too large (~0.1 V at 99 °C) to expect substantial arene oxidation. However, the formation of moderate amounts (1–10%) of radical cation may be expected from their data and, indeed, we[19] observed an intense ESR spectrum of the pyrene radical cation in $SbCl_3$–8 mol % $AlCl_3$.

added $AlCl_3$ or Me_4NCl.

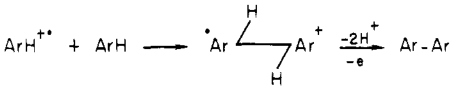
It will be noted from the above that for a given arene, the conditions under which the reaction

$$ArH + {}^{1}/_{3}SbCl_3 \rightarrow ArH^{+\cdot} + {}^{1}/_{3}Sb + Cl^- \qquad (2)$$

occurs are the same as those under which the self-protonation reactions typified by eq 1 occur. These results, including the isolation of stoichiometric quantities of Sb metal, suggest that the arene radical cation is an important reactive intermediate. Thus, the strong protonic acid responsible for self-protonation may have been derived from the coupling of radical cations[21] as in reaction


(3)

3 or from the electrophilic attack of radical cations on yet unreacted arene molecules as in reaction 4.[21]


(4)

We have described an unusual arene self-protonation reaction which takes place in an aprotic $SbCl_3$–$AlCl_3$ melt and which is driven by the stoichiometric reduction of $SbCl_3$ to Sb metal. In addition we have presented evidence that the reaction begins with the oxidation of the arene to its radical cation by the solvent, $SbCl_3$, and that the role of the $AlCl_3$ is to enhance the oxidizing power of the $SbCl_3$.

Acknowledgments. We appreciate the assistance of L. L. Brown with the NMR measurements, M. V. Buchanan with the mass spectroscopy measurements, H. L. Yakel with the X-ray diffraction study, and L. O. Gilpatrick with the product separations and identifications. We also appreciate valuable discussions with M. L. Poutsma and J. Brynestad. This research was sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corp.

---

[21] Wen, Long-Sing; Kovacic, P. *Tetrahedron* **1978**, *34*, 2723, and references cited therein.

Redox-Photosensitized Reactions. 5.[1] Redox-Photosensitized Ring Cleavage of 1,1a,2,2a-Tetrahydro-7*H*-cyclobut[*a*]indene Derivatives: Mechanism and Structure–Reactivity Relationship

Tetsuro Majima, Chyongjin Pac,* and Hiroshi Sakurai

Contribution from The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan. *Received December 7, 1979*

Abstract: The mechanistic aspects of the redox-photosensitized chain cycloreversion of *trans,syn*-indene dimer **1** have been investigated in detail. The π complex of **1** with the cation radical of phenanthrene (and selected other aromatic hydrocarbons) that is generated by photochemical electron transfer with *p*-dicyanobenzene has been shown to be a key intermediate by way of which the cycloreversion of **1** rapidly occurs without the formation of its cation radical; the rate constant for the cycloreversion has been determined to be $1 \times 10^9\ s^{-1}$. Redox photosensitization has been applied to the other related compounds and it has been found that the cyclobutanes which can undergo redox-photosensitized ring cleavage possess the phenyl group at C_2. The importance of through-bond interactions between the two π-electron systems is discussed.

Introduction

Electron transfer is an important photochemical process of exciplex formation systems in polar solvents;[2,3] the chemistry of photogenerated ion radicals has now received considerable attention.[4-7] In a previous paper,[8] we reported that in aromatic hydrocarbon (S)–*p*-dicyanobenzene (DCNB)–acetonitrile systems a novel type of photosensitization occurs which causes ionic reactions of furan and olefins (D). We now call this photosensitization redox photosensitization, since the initiation process is the photochemical electron transfer (photoredox) reaction from S to DCNB[8-10] and since an important intermediate is the cation radical of S ($S^{+}\cdot$) which may act as a redox carrier. The final products would be interpreted to arise from the cation radical of D. However, the redox-photosensitized reactions can occur even in cases where complete hole transfer from $S^{+}\cdot$ to D which gives the cation radical of D is substantially endothermic. Therefore, we assumed the intervention of a π complex formed between $S^{+}\cdot$ and D as a key intermediate.[8]

Thus, redox photosensitization is closely related to the chemical nature of photogenerated $S^{+}\cdot$ and has been applied to other re-

---

[1] Part 4: T. Majima, C. Pac, J. Kubo, and H. Sakurai, *Tetrahedron Lett.*, 377 (1980).

[2] A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).

[3] M. Ottolenghi, *Acc. Chem. Res.*, **6**, 153 (1973); P. Froelich and E. L. Wehry in "Modern Fluorescence Spectroscopy", Vol. 2, E. L. Wehry, Ed., Plenum Press, New York, 1976, pp 381-6.

[4] C. Pac and H. Sakurai, *Tetrahedron Lett.*, 3829 (1969); K. Mizuno, C. Pac, and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 553 (1975); K. Mizuno, H. Okamoto, C. Pac, and H. Sakurai, *ibid.*, 839 (1975).

[5] R. A. Neunteufel and D. R. Arnold, *J. Am. Chem. Soc.*, **95**, 4080 (1973); D. R. Arnold and A. J. Maroulis, *ibid.*, **99**, 7355 (1977), and references cited therein.

[6] J. A. Barltrop, *Pure Appl. Chem.*, **33**, 179 (1973).

[7] A. Ledwith, *Acc. Chem. Res.*, **5**, 133 (1972); S. Farid, S. H. Hartman, and T. R. Evans in "The Exciplex", M. Gordon and W. R. Ware, Eds., Academic Press, New York, 1975, p 327; T. R. Evans, R. Wake, and O. Jaeckie, *ibid.*, p 345; K. Mizuno, R. Kaji, H. Okada, and Y. Otsuji, *J. Chem. Soc., Chem. Commun.*, 594 (1978).

[8] C. Pac, A. Nakasone, and H. Sakurai, *J. Am. Chem. Soc.*, **99**, 5806 (1977).

[9] T. Asanuma, T. Gotoh, A. Tsuchida, M. Yamamoto, and Y. Nishijima, *J. Chem. Soc., Chem. Commun.*, 485 (1977).

[10] S. Tazuke and N. Kitamura, *J. Chem. Soc., Chem. Commun.*, 515 (1977).

0002-7863/80/1502-5265$01.00/0